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Theoretical studies on bond dissociation enthalpies for model compounds of typical plastic polymers

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Abstract. The polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), polyethylene terephthalate (PET), bisphenol A polycarbcconate (PC) comprise above 80% of plastic polymers. The bond dissociation enthalpies for model compounds of the six typical plastic polymers were calculated by using density functional theory methods, and the possible degradation mechanisms of these plastic polymers were proposed. The degradation of PE and PP is mainly main-chain random scission mechanism; the PS degradation is mainly zipper scission and main-chain random scission mechanism; the PVC degradation is mainly branched-chain scission mechanism; the PET and PC decompose mainly through C-O homolytic cleavage, C-C homolytic cleavage and concerted reaction.

1. Introduction

Plastic plays an important role in improving people's living standards over the past several decades. It is a key of innovation of many products in various sectors such as packaging, electronic, construction, automotive, healthcare and others [1]. However, the applications of these plastic goods have continuously given rise to plastic waste pollution problems around the world. At present, most of these plastic wastes are disposed of through dumping into landfills or burning in incinerators along with other solid wastes [2]. But these conventional methods will be phased out in the near future due to the serious environmental pollution problems they lead to. There is a great need to deploy and develop new environmentally friendly and cost-effective waste plastic management technologies as currently used disposal options become less viable. Among these, thermochemical conversion to energy resources has been a significant way to use such waste plastics effectively and to meet with the growing demand from the energy sector [3].

Pyrolysis, the thermal decomposition of organic materials in the absence of oxygen at a mediate temperature [4], is considered as an environmentally friendly and widely used method and producing renewable energy from biomass [5]-[8]. Extensive researches were performed worldwide for the production of alternative fuels or chemicals from waste plastics through the pyrolysis [9]-[14]. The previous studies on mechanism of plastics thermal decomposition mainly focused on experimental studies to explore the distribution of products in different pyrolysis conditions. However, there are few researches about chemical reactions and formation mechanisms of the main products during plastics thermal decomposition. In the process of thermal decomposition, the free radical reaction is considered to be one of the main pyrolysis mechanisms [15], [16]. Bond dissociation enthalpy is an

important thermodynamic quantity that can exemplify chemical activity of free radicals reaction, and the smaller the bond dissociation enthalpy is, the more easily the bond is broken [17]. So the theoretical studies on bond dissociation enthalpies contribute to the further understanding of thermal decomposition mechanism of plastic polymers. In this study, the bond dissociation enthalpies (BDE) for model compounds of six typical plastic polymers (as shown in Figure 1) were calculated by using density functional theory (DFT) methods, and the possible formation pathways of main products in the pyrolysis processes were analysed.

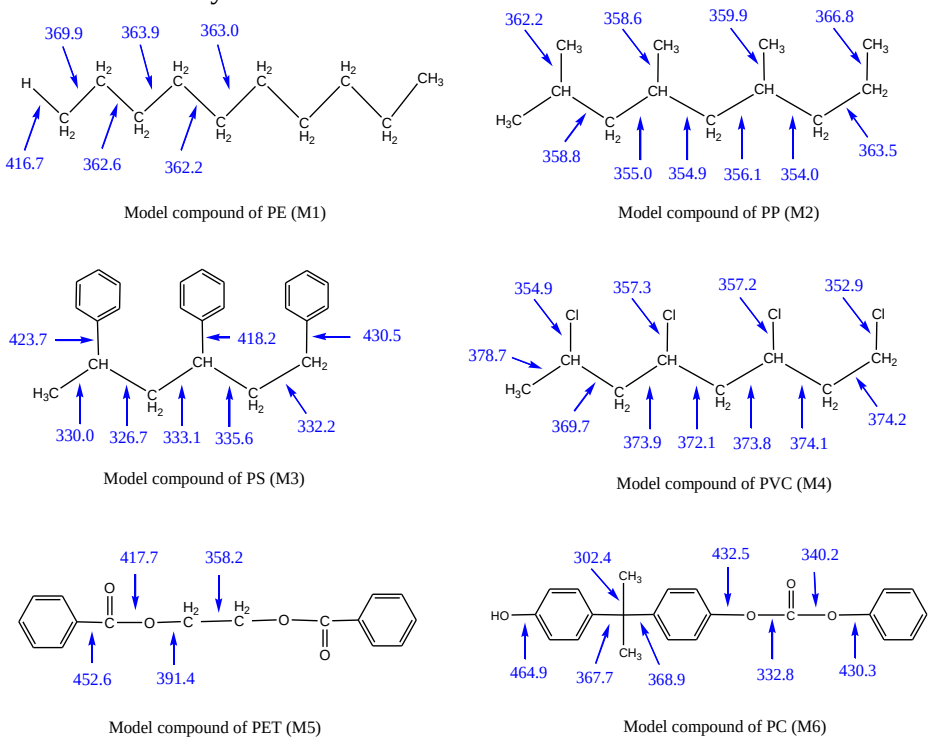

Figure 1. Model compounds of six typical plastic polymers (M1~M6) and the BDE values marked in blue, calculated by using M06-2X/6-31++G(d,p) (kJ/mol).

2. Calculation methods

All calculations were completed using Gaussian 09 suite of programs [18]. The literatures [19], [20] reported that the M06-2X and B3P86 functionals was superior to other functionals for the reproduction of BDE. So the equilibrium geometries of reactants, intermediates, transition states and products were optimized by employing density functional theory methods M06-2X [21] and B3P86 [22] with the 6-31++G(d,p) basis set. Standard thermodynamic parameters at 298 K, including zero-point energy correction (ZPE), were obtained by vibrational frequency calculations. Bond dissociation enthalpy is calculated as [23]:

$$\mathrm{BDE}_{298}(\text{R-X}) = H_{298}(\text{R}) + H_{298}(\text{X}) - H_{298}(\text{R-X}) \tag{1}$$

where H_{298} is the enthalpies of formation of the molecule and radical species, which is calculated using the following equation [24]:

$$H_{298} = E + ZPE + H_{trans} + H_{rot} + H_{vib} + RT \tag{2}$$

where ZPE is the zero point energy. H_{trans}, H_{rot} and H_{vib} are the standard temperature correction term calculated using the equilibrium statistical mechanics with harmonic oscillator and rigid rotor approximations.

3. Results and discussion

Calculations of bond dissociation enthalpies contribute to the understanding of free radicals reaction processes. Figure 1 marks the BDE values of the major bonds of model compounds of six typical

plastic polymers (M1~M6), calculated by using M06-2X with the 6-31++G(d,p) basis set. Table 1 lists the BDE values of the major bonds of M1~M6, calculated at M06-2X/6-31++G(d,p) level and at B3P86/6-31++G(d,p) level. The average BDE value of main-chain C-C bond for model compound of polyethylene (PE) at M06-2X/6-31++G(d,p) level is 364.3 kJ/mol, and that of main-chain C-C bond for M1 at B3P86/6-31++G(d,p) level is 350.9 kJ/mol. The average BDE value of main-chain C-C bond for model compound of polypropylene (PP) at M06-2X/6-31++G(d,p) level is 357.1 kJ/mol, and that of main-chain C-C bond for M2 at B3P86/6-31++G(d,p) level is 329.5 kJ/mol; but the average BDE value of branched-chain C-CH3 bond for model compound of polypropylene (PP) at M06-2X/6-31++G(d,p) level is 361.9 kJ/mol, and that of branched-chain C-CH3 bond for M2 at B3P86/6-31++G(d,p) level is 342.6 kJ/mol. The average BDE value of main-chain C-C bond for model compound of polystyrene (PS) at M06-2X/6-31++G(d,p) level is 331.5 kJ/mol, and that of main-chain C-C bond for M3 at B3P86/6-31++G(d,p) level is 291.7 kJ/mol; but the average BDE value of branched-chain C-Caromatic bond for model compound of polystyrene (PS) at M06-2X/6-31++G(d,p) level is 424.1 kJ/mol, and that of branched-chain C-Caromatic bond for M3 at B3P86/6-31++G(d,p) level is 395.9 kJ/mol. So the homolytic cleavage of main-chain C-C bond in the PP and PS pyrolysis is the main degradation pathway. The average BDE value of main-chain C-C bond for model compound of polyvinyl chloride (PVC) at M06-2X/6-31++G(d,p) level is 373.8 kJ/mol, and that of main-chain C-C bond for M4 at B3P86/6-31++G(d,p) level is 345.8 kJ/mol; but the average BDE value of branched-chain C-Cl bond for M4 at M06-2X/6-31++G(d,p) level is 355.6 kJ/mol, and that of branched-chain C-Cl bond for M4 at B3P86/6-31++G(d,p) level is 343.7 kJ/mol. By comparing the BDE values, the order of the BDE value of the weakest bond for M1~M4 is as follows: PS < PVC < PP < PE. In the pyrolysis of PE, PP and PS, the free radical reaction mechanism is considered to be the main pyrolysis mechanism. For free-radical reactions, the bond dissociation enthalpies may serve as approximations to the activation energies [6]. In the PVC pyrolysis, PVC was initially dehydrochlorinated to generate HCl by concerted reaction mechanism [25], and the activation energy in concerted reaction is significantly lower than that in free radical reaction. Therefore, we can infer that the order of the thermal stability is as follows: PVC < PS < PP < PE, which is in accordance with the related experimental result [26].

Table 1. The BDE values of the major bonds of model compounds of six typical plastic polymers (M1~M6)

		BDE									
M1	M062X	416.7	369.9	362.6	363.9	362.2	363.0				
	B3P86	422.6	359.2	346.6	349.4	348.4	351.0				
M2	M062X	366.8	359.9	358.6	362.2	363.5	354.0	356.1	354.9	355.0	358.8
	B3P86	353.7	337.4	336.8	342.4	341.9	325.7	327.3	325.9	326.5	329.8
M3	M062X	430.5	418.2	423.7	332.2	335.6	333.1	326.7	330.0		
	B3P86	405.3	392.0	390.4	295.6	288.4	288.2	285.6	300.7		
M4	M062X	352.9	357.2	357.3	354.9	374.2	374.1	373.8	372.1	373.9	369.7
	B3P86	346.4	343.1	343.2	342.2	351.2	343.6	342.4	341.6	342.8	340.6
M5	M062X	452.6	417.7	391.4	358.2						
	B3P86	438.0	392.5	342.1	338.5						
M6	M062X	430.3	340.2	332.8	432.5	368.9	367.7	302.4	464.9		
	B3P86	385.4	307.9	302.3	389.2	329.2	328.9	267.1	462.0		

For the model compound of polyethylene terephthalate (PET), the BDE value of C-C bond is the lowest, 358.2 kJ/mol at M06-2X/6-31++G(d,p) level (338.5 kJ/mol at B3P86/6-31++G(d,p) level), and the BDE value of O-C bond is the second lowest, 391.4 kJ/mol at M06-2X/6-31++G(d,p) level (342.1 kJ/mol at B3P86/6-31++G(d,p) level). For the model compound of bisphenol A polycarbonate (PC),

the BDE value of C-CH_c bond is the lowest, 302.4 kJ/mol at M06-2X/6-31++G(d,p) level (267.1 kJ/mol at B3P86/6-31++G(d,p) level), and the BDE value of O-Ccarbonyl bond is the second lowest, 332.8 kJ/mol at M06-2X/6-31++G(d,p) level (302.3 kJ/mol at B3P86/6-31++G(d,p) level). For PET and PC, it is clear that the C-C bond dissociation is easiest, followed by C-O dissociation of carbonate group. However, the carbonate group is reactive easily with water or alcohol, so the degradation may not exactly follow the bond dissociation enthalpies [10].

The BDE values calculated at M06-2X/6-31++G(d,p) level are higher than those at B3P86/6-31++G(d,p) level, but the variation trends of BDE values at two levels are similar. Comparing with the method B3P86, M06-2X is more accurate according to many other studies about carbohydrates systems [19], [20].

Based on related experimental results and experiences, we propose various possible thermal degradation pathways. Figure 2 depicts the proposed degradation reaction pathways in the pyrolysis process of PE and PP. The PE and PP degradation mechanism is mainly main-chain random scission, namely macromolecular main-chain cracks randomly to generate various free radicals. These free radicals further decompose into various products through intramolecular or intermolecular hydrogen transfer reaction. As shown in Figure 2, PE or PP can decompose into the radicals R1 and R2 through random cleavage of the C-C bond. The radicals R1 and R2 can further decompose into the smaller radicals and products such as ethylene, propylene, butane, ethane, propane and others.

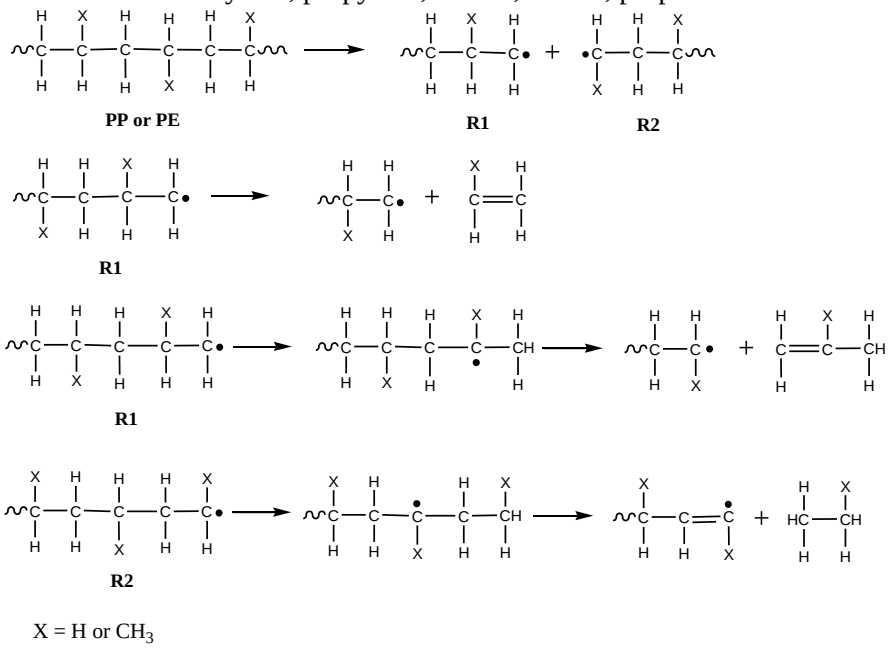

Figure 2. Formation mechanism of various main pyrolysis products in the pyrolysis of PE and PP

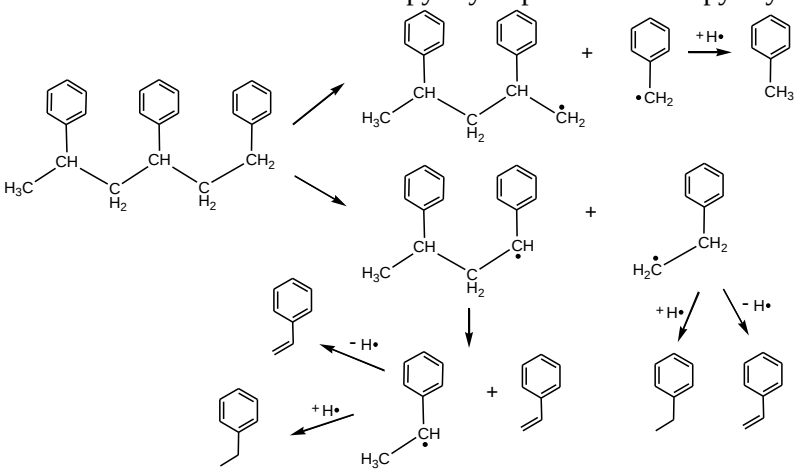

Figure 3. Proposed degradation pathways in the pyrolysis process of model compound of PS (M3)

Figure 3 describes the proposed degradation reaction pathways in the pyrolysis process of model compound of PS. The PS degradation mechanism is mainly zipper scission and main-chain random scission, and the PS pyrolysis produced a very high yield of monomer styrene due to zipper scission reaction. As shown in Figure 3, the model compound of polystyrene (M3) can decompose to form a free radical and benzyl, and the benzyl can be further converted into methylbenzene through a hydrogenation reaction. M3 can also decompose to form a free radical and phenyl ethyl, and the free radical can further decompose to form styrene and a smaller radical. The phenyl ethyl can be further converted into phenylethane through a hydrogenation reaction, or into styrene through a dehydrogenation reaction.

Figure 4 depicts the proposed degradation pathways in the pyrolysis process of model compound of PVC. The PVC degradation mechanism is mainly branched-chain scission, namely the elimination reaction of HCl occurs and then the main-chain is converted into the conjugated dienes chain, which can be further converted into benzene compound, often accompanied by crosslinking reaction.

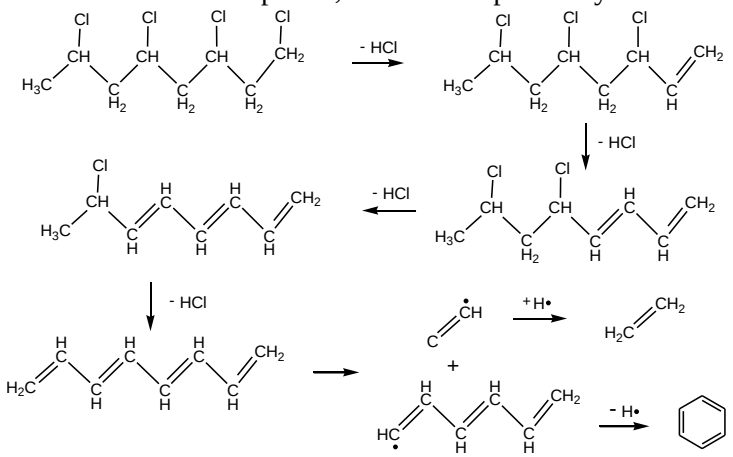

Figure 4. Proposed degradation pathways in the pyrolysis process of model compound of PVC (M4)

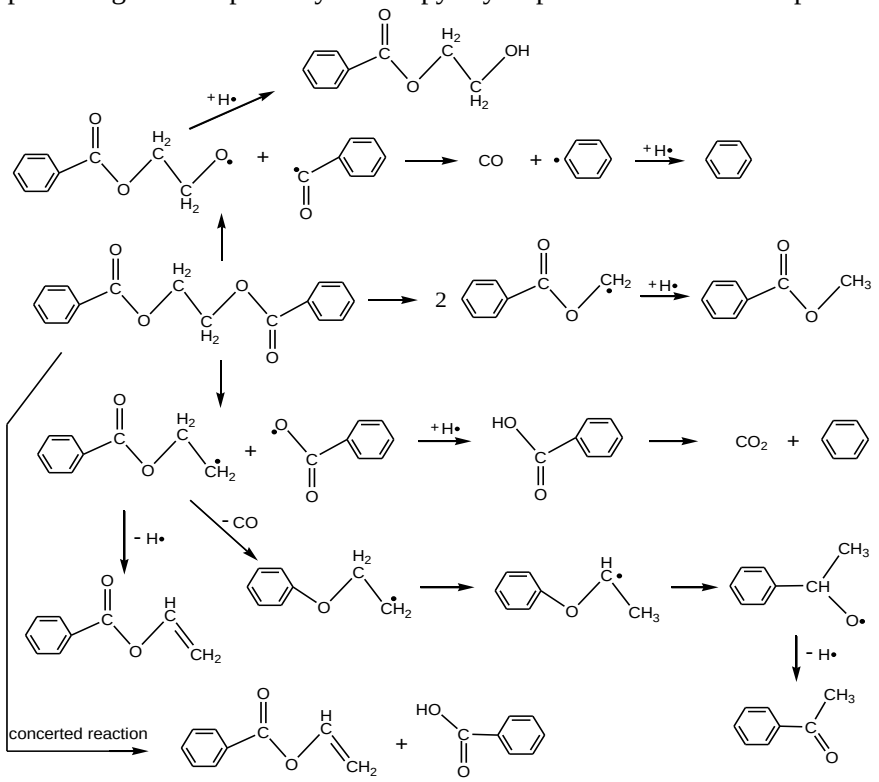

Figure 5. Proposed degradation pathways in the pyrolysis process of model compound of PET (M5)

Figure 5 depicts the proposed degradation pathways in the pyrolysis process of model compound of PET (M5). M5 can decompose into two same radicals through C-C homolytic cleavage, and the radical can be further converted into benzoic acid methyl ester. M5 can also decompose into the various radicals through C-O homolytic cleavage, and these radicals can further decompose into various products such as CO_2, CO, benzene, benzoic acid, acetophenone, 1-hydroxyl ethyl benzoate, vinyl benzoate and others. M5 can also decompose into benzoic acid and vinyl benzoate through concerted reaction, which is similar to the dehydration reaction.
Figure 6 describes the proposed degradation reaction pathways in the pyrolysis process of model compound of PC (M6). M6 can decompose into two radicals through C-O homolytic cleavage, and the radicals can further decompose into CO_2, CO and bisphenol A. The calculation results of the BDE show that methyl scissions occur easily in the isopropylidene linkage, and 1,1-bis(4-hydroxyphenyl)-ethane can be easily formed through C-CH_3 homolytic cleavage. M6 can also directly decompose into bisphenol A and carbonate through hydrolysis reaction. The carbonate can further decompose to form CO_2 and phenol by a decarboxylation reaction.

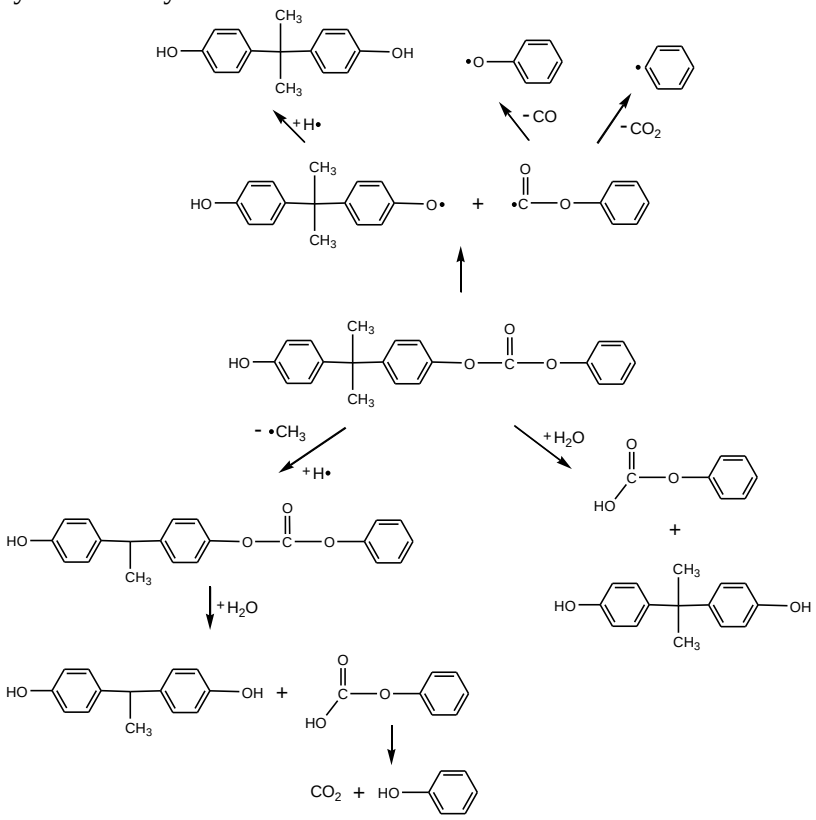

Figure 6. Proposed degradation pathways in the pyrolysis process of model compound of PC (M6)

4. Conclusions

In the present study, density functional theory methods M062X and B3P86 were used to investigate the bond dissociation enthalpies for model compounds of the six typical plastic polymers. The BDE values calculated at M06-2X/6-31++G(d,p) level are higher than those at B3P86/6-31++G(d,p) level, and M06-2X is more accurate according to many other studies about carbohydrates systems. On the basis of computational results, the order of the thermal stability for four kinds of polyolefins is as follows: PVC < PS < PP < PE. The possible formation pathways of main products in the pyrolysis of six plastic polymers were proposed. PE and PP degradation mechanism is mainly main-chain random scission; PS degradation mechanism is mainly zipper scission and main-chain random scission, and the PS degradation produced a very high yield of monomer styrene; PVC degradation mechanism is mainly branched-chain scission, in which the elimination of HCl occurs and then the conjugated

dienes chain is formed; PE and PP pyrolysis processes is more complicated, and cPET and PC decompose mainly through C-O and C-C homolytic cleavage and concerted reaction.

5. Reference

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